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## Contactless analysis of surface passivation and charge transfer at the $\text{TiO}_2$ –Si interface<sup>†</sup>

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Transition metal oxides are pivotal in enhancing surface passivation and facilitating charge transfer (CT) in silicon based photonic devices, improving their efficacy and affordability through interfacial engineering. This study investigates  $\text{TiO}_2$ /Si heterojunctions prepared by atomic layer deposition (ALD) with different pre-ALD chemical and post-ALD thermal treatments, exploring their influence on the surface passivation and the correlation with the CT at the  $\text{TiO}_2$ –Si interface. Surface passivation quality is evaluated by the photoconductance decay method to study the effective carrier lifetime, while CT from Si to  $\text{TiO}_2$  is examined by transient reflectance spectroscopy. Surprisingly, the as-deposited  $\text{TiO}_2$  on HF-treated n-Si (without interfacial  $\text{SiO}_x$ ) demonstrates superior surface passivation with an effective lifetime of 1.23 ms, twice that of  $\text{TiO}_2$ / $\text{SiO}_x$ /n-Si, and a short characteristic CT time of 200 ps, tenfold faster than that of  $\text{TiO}_2$ / $\text{SiO}_x$ /n-Si. Post-ALD annealing at temperatures approaching the  $\text{TiO}_2$  crystallization onset re-introduces the  $\text{SiO}_x$  layers in HF-treated samples and induces chemical and structural changes in all the samples which decrease passivation and prolong the CT time and are hence detrimental to the photonic device performance.

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### 1. Introduction

Efficiently harnessing renewable energy is crucial, and silicon's (Si) abundance on Earth, coupled with its favorable 1.1 eV band gap, allows it to operate effectively within the visible to NIR range of the solar spectrum.<sup>1–3</sup> As a result, it has become a fundamental component in photovoltaic (PV) cells<sup>4,5</sup> and photoelectrochemical (PEC) cells.<sup>6,7</sup> Among these, crystalline silicon (c-Si) based devices have emerged as highly attractive and promising devices for cost-effective, green, and sustainable renewable energy production. However, the performance of state-of-the-art c-Si-based PV and PEC devices is often limited by recombination of their surfaces and interfaces which leads to a loss in their photogenerated charge carrier collection and thus a reduction in their energy conversion efficiency. The reduction of such recombination, commonly referred to as surface passivation, can be achieved by the combined effect

of the reduction in the trap states present at the surface *via* a chemical component, and the reduction in the charge carriers available for a recombination process *via* a field effect component.<sup>8</sup> Passivating layers have demonstrated significant potential in enhancing the performance of c-Si solar cells, enabling their theoretical efficiency limit to approach approx. 29.43%.<sup>9–11</sup>

Transition metal oxides (TMOs) including  $\text{ZnO}$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{CuO}$  have attracted great interest as potential passivating layers for silicon surfaces and interfaces, offering tunable optoelectronic properties with cost-effective deposition methods.<sup>12–16</sup> Sahoo *et al.* deposited 1 nm  $\text{CuO}$  as a tunneling oxide passivating layer over Si and improved the minority carrier lifetime of the Si-based solar cells.<sup>14</sup> Gerling *et al.* deposited  $\text{MoO}_3$ ,  $\text{WO}_3$  and  $\text{V}_2\text{O}_5$ , over n-Si and improved the lifetime of carriers up to 240, 142, and 4.5  $\mu\text{s}$ , respectively.<sup>17</sup> Loo *et al.* deposited a 75 nm  $\text{ZnO}$  film over n-Si by ALD and improved the carrier lifetime up to 312  $\mu\text{s}$ .<sup>18</sup> However, among them one promising material is  $\text{TiO}_2$  which has excellent chemical stability, dielectric properties, and high transparency that reduce problems such as surface parasitic absorbance.<sup>19,20</sup> Atomic layer deposition (ALD) has emerged as a powerful method to grow  $\text{TiO}_2$  thin films on Si substrates for passivation application.<sup>21–23</sup> It has been employed extensively since it allows growth of pinhole-free high quality  $\text{TiO}_2$  thin films at mono layer thickness with controllable and favorable optical properties.<sup>19,21,24,25</sup> The properties of ALD  $\text{TiO}_2$  thin films can

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be affected by substrate pre-treatments, precursor choice, growth parameters and post-deposition treatments. Recent research has demonstrated that by depositing a  $\text{TiO}_2$  surface passivation layer on Si by ALD using  $\text{TiCl}_4$  and  $\text{H}_2\text{O}$  precursors, the effective minority carrier lifetimes increase above 10 ms with decreasing ALD growth temperature, which is due to the increasing amount of ALD precursor traces (Cl and H) within  $\text{TiO}_2$  films as the growth temperature decreases.<sup>26</sup> Previous studies show that the quality of surface passivation by amorphous  $\text{TiO}_2$  thin film is sensitive to Si wafer pre-treatments and thus can be significantly optimized and increased by applying precisely conditioned annealing, particularly through a pre-ALD growth of a  $\text{SiO}_x$  interlayer.<sup>20,27–29</sup> However, post-ALD deposition, the increased annealing temperature and duration can lead to a noticeable decline in surface passivation quality due to  $\text{TiO}_2$  crystallization and associated breaking of Si–O–Ti bonds at the  $\text{TiO}_2$ –Si interface.<sup>28,29</sup>

In addition to surface passivation, TMOs can also be applied over Si as corrosion protection layers. In that case, meticulous attention should be paid to the ultra-fast charge transfer (CT) (in the ps–ns time domain) from the semiconductor photoabsorber to the TMO coating, as it can significantly impact the performance of PV devices. In high-efficiency PV cells with passivating contacts, majority carriers traverse the passivating TMO layer to reach the metal contact, and similarly, in PEC cells, carriers navigate through the TMO layer to access the reactive surface. Since  $\text{TiO}_2$  exhibits hole-blocking and electron-transporting capabilities, it can be used simultaneously for surface passivation and CT in both PV and PEC devices.<sup>30–32</sup> However, earlier studies often show a trade-off between the surface passivation and CT at the  $\text{TiO}_2$ –Si interface. For example, the presence of a thin  $\text{SiO}_x$  interfacial layer can improve the passivation quality but it limits the CT process.<sup>33–35</sup> Therefore, investigating and understanding the CT dynamics of photo-excited charges from Si to  $\text{TiO}_2$ <sup>33,36</sup> across the  $\text{TiO}_2$ –Si interface is crucial for optimizing the design and performance of the devices that rely on these materials. Femtosecond transient reflectance (TR) spectroscopy is a time-resolved technique used to extract information about the population of photogenerated charge carriers. This technique allows us to map out charge-transfer pathways by identifying decay features in the spectra. Consequently, information about the quenching and transfer of charge carriers, along with their corresponding lifetimes, which is relevant to photonic applications, can be extracted within femtosecond to nanosecond timescales.<sup>37–39</sup> Herein, we have employed TR spectroscopy to get a complete picture of the phenomena related to ultrafast changes in reflectivity, diffusion of carriers, and particularly the CT process occurring at the interface in our  $\text{TiO}_2$ /Si heterojunctions.

In this study, we prepare high-quality ALD  $\text{TiO}_2$  thin films at 120 °C using  $\text{TiCl}_4$  and  $\text{H}_2\text{O}$  precursors on both p- and n-type Si substrates, with different pre-ALD chemical and post-ALD thermal treatments. This ALD  $\text{TiO}_2$  coating is amorphous and contains an elevated amount of precursor traces (~1 at% H and Cl).<sup>40</sup> The post-ALD thermal treatments were carefully selected to control the diffusion of H, Cl, and O within the

$\text{TiO}_2$  while maintaining the amorphous phase. The resulting surface passivation quality of the  $\text{TiO}_2$ /Si heterojunctions is studied using the contactless quasi steady state photoconductance (QSSPC) method to measure the minority carrier lifetime. Furthermore, to gain insights on the CT dynamics across the  $\text{TiO}_2$ –Si interface and transport of electrons in the  $\text{TiO}_2$  layer, contactless TR spectroscopy is utilized. Additionally, a Kelvin-probe is applied to study the Si surface barrier with  $\text{TiO}_2$  and how it contributes to the surface passivation and the CT in  $\text{TiO}_2$ /Si heterojunctions. The topography of the samples is analyzed with AFM to examine and understand the structural and compositional changes occurring within the  $\text{TiO}_2$  thin films as a result of annealing and further how these changes contribute to the surface passivation and the CT process. Our results provide new insights on engineering effective surface passivation with optimized CT at the  $\text{TiO}_2$ –Si interface, thus, paving the way for achieving highly efficient Si-based PV and PEC devices.

## 2. Synthesis

Boron-doped (p-Si samples) and phosphorus-doped (n-Si samples) single-side-polished float-zone c-Si wafers (100 mm diameter, (100) orientation, 1–5 Ω cm resistivity, and 280 μm thickness) were used as substrates. Initially, all the wafers underwent thermal oxidation at 1050 °C to deactivate bulk defects.<sup>34,41</sup> After removing the thermal oxide layer by a 1% HF dip, the wafers were subsequently cleaned using a standard process consisting of RCA1, HF dip, and RCA2. This resulted in a chemical  $\text{SiO}_x$  surface layer<sup>42</sup> with a thickness of 1.8 nm determined by ellipsometry, assuming a refractive index of 1.465 at 632.8 nm. However, this thickness is slightly overestimated and actual thickness should be thinner than <1 nm.<sup>43</sup> Half of the samples were subjected to a second HF dip after the RCA2 step just before the ALD growth of  $\text{TiO}_2$  to prepare  $\text{TiO}_2$ /Si samples without an interfacial  $\text{SiO}_x$  layer.<sup>44,45</sup> Saari *et al.* have previously found out by XPS that the  $\text{TiO}_2$ /Si interface remains free from  $\text{SiO}_x$  for the thermal ALD  $\text{TiO}_2$  process using TDMAT and  $\text{H}_2\text{O}$  precursors at 100 °C.<sup>44</sup>

Right after the chemical treatments, the samples were immediately transferred to the ALD chamber to deposit the  $\text{TiO}_2$  thin films on both sides of the wafers. The deposition was done by using a thermal ALD tool (Beneq TFS-500), which was pumped to vacuum, heated to 120 °C and stabilized for 1 hour before starting deposition.  $\text{TiCl}_4$  was employed as the Ti precursor and water ( $\text{H}_2\text{O}$ ) was employed as the oxidant.<sup>40</sup> A single ALD cycle consisted of a 200 ms  $\text{TiCl}_4$  precursor pulse and a 150 ms  $\text{H}_2\text{O}$  oxidant pulse, each followed by a 3 s  $\text{N}_2$  purge. The deposition rate was estimated to be 0.43 Å per cycle and in total 1200 cycles were used for depositing 54 nm thick films, as determined by ellipsometry and confirmed by SEM (Fig. S1, ESI†).

The thickness of the  $\text{TiO}_2$  films was optimized for TR measurements, in order to acquire a suitable interference pattern to increase the signal strength of transferred carriers while retaining the same interface and CT rate. The steady-state reflectance spectra of all the as-deposited  $\text{TiO}_2$ /Si heterojunctions



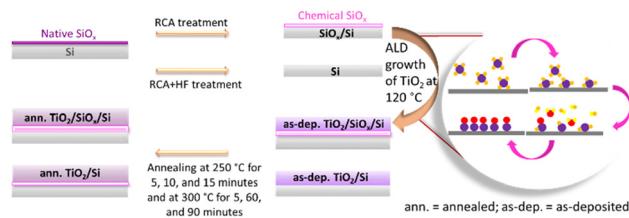


Fig. 1 Synthesis of  $\text{TiO}_2$  on Si substrates by ALD using  $\text{TiCl}_4$  and  $\text{H}_2\text{O}$  as precursor materials.

are shown in the ESI,<sup>†</sup> Fig. S2 confirming similarity of the samples, *i.e.*, the HF-treatment had only little effect on the  $\text{TiO}_2$  film thickness.<sup>33</sup> Full wafers were cut to quarters and then the samples were thermally annealed in a tube furnace (ATV PEO-601) under  $\text{N}_2$  ambience at 250 °C for 5, 10, and 15 minutes. Despite the HF treatment, some interfacial  $\text{SiO}_x$  grows between Si and  $\text{TiO}_2$  during the thermal annealing process.<sup>29</sup> Saari *et al.* have shown that the thickness of interfacial  $\text{SiO}_x$  increases linearly with temperature in the range of 200–550 °C.<sup>44</sup> However, one quarter from each wafer was left without the thermal annealing of the as-deposited (as-dep.)  $\text{TiO}_2/\text{Si}$  heterojunctions, to study how the thermal annealing affects both the surface passivation and CT properties. A schematic of sample preparation is shown in Fig. 1. Similarly, to study the effect of increasing the annealing temperatures and durations,  $\text{TiO}_2/\text{Si}$  heterojunctions were annealed at 300 °C for 5, 60, and 90 minutes while one sample was left without annealing (as-deposited).

### 3. Results and discussion

#### 3.1. Surface passivation provided by $\text{TiO}_2$

To study the passivation effect of  $\text{TiO}_2$  thin films on Si, effective carrier lifetimes,  $\tau_{\text{eff}}$ , of both n-type and p-type silicon wafers with and without HF treatment are measured. Assuming that the bulk substrate has infinite lifetime, the upper limit of the surface recombination velocity (SRV),  $S_{\text{eff,max}}$ , has been estimated. It can be defined as a rate at which carriers recombine at the surface and in the case of symmetrical samples it can be calculated as  $S_{\text{eff,max}} \approx \frac{W}{2\tau_{\text{eff}}}$ , where  $W$  is the wafer thickness.<sup>46</sup>

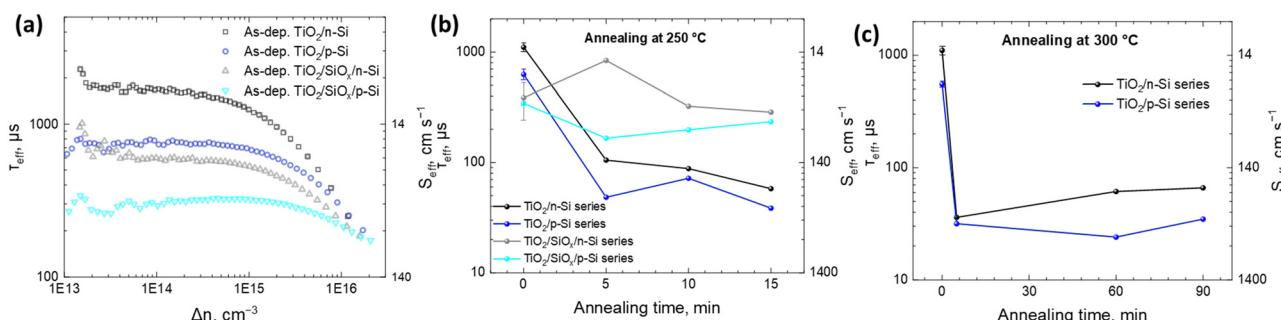


Fig. 2 (a) Injection-level dependent effective lifetimes for Si wafers passivated by 54 nm thin films of (a) as-deposited  $\text{TiO}_2$ , (b) annealed  $\text{TiO}_2$  films at 250 °C, and (c) annealed  $\text{TiO}_2$  films at 300 °C for different durations. The corresponding surface recombination velocities ( $S_{\text{eff}}$ ) are also shown on the right y-axis.

Fig. 2a depicts typical injection-dependent effective lifetime results and the determined  $S_{\text{eff,max}}$  for all the as dep.  $\text{TiO}_2/\text{Si}$  and  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples. Interestingly, the HF-treated as dep. samples exhibit higher lifetimes than their counterparts, the  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples. Among all the samples, the  $\text{TiO}_2/\text{n-Si}$  sample shows the best passivation performance having a maximum lifetime of approximately 1.23 ms. At a carrier injection level of  $1.0 \times 10^{15} \text{ cm}^{-3}$ , the corresponding  $S_{\text{eff,max}}$  is around  $11.4 \text{ cm s}^{-1}$ . This result is comparable to the values reported earlier for ALD  $\text{TiO}_2$  passivated silicon.<sup>26</sup> Table S1 (ESI<sup>†</sup>) summarizes the lifetimes and the corresponding  $S_{\text{eff,max}}$  for all the as-dep.  $\text{TiO}_2/\text{Si}$  and  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples.

The HF-treated as-dep.  $\text{TiO}_2/\text{p-Si}$  shows a higher recombination rate of  $20.3 \text{ cm s}^{-1}$  as compared to the as-dep.  $\text{TiO}_2/\text{n-Si}$ , which shows  $11.4 \text{ cm s}^{-1}$ . For reference, for HF-treated (Si-H terminated/H passivated Si surface)<sup>47</sup> n- and p-Si, the  $S_{\text{eff,max}}$  values were  $636.4$  and  $241.4 \text{ cm s}^{-1}$ , respectively. This means that with the deposition of  $\text{TiO}_2$  thin films, the  $S_{\text{eff}}$  values are minimized for both n- and p-Si. The difference in  $S_{\text{eff}}$  between n- and p-Si can be accounted for by different surface passivation properties, as the bulk of both substrates has been proven to be of high quality ( $\tau_{\text{eff}}$  above 10 ms) in separate experiments using  $\text{Al}_2\text{O}_3$  surface passivation.<sup>48,49</sup> Therefore, the dopant type in Si is found to have a minor influence on the achievable passivation levels. Loo *et al.* also observed a minor influence of the dopant type on the achievable passivation levels.<sup>18</sup> Moreover, the results reveal a consistent pattern where the presence of RCA2 oxide increases the SRV for both p-type and n-type wafers underscoring the detrimental impact of this oxide on the passivation performance, as listed in Table S1 (ESI<sup>†</sup>). This observed trend is consistent with prior research, *e.g.*, carried out by Mochizuki *et al.*<sup>20</sup> and Liao *et al.*,<sup>29</sup> which attributes the increase in  $S_{\text{eff}}$ , in the case of amorphous  $\text{TiO}_2$  coatings, to the increase in the interfacial defect density upon the formation of  $\text{SiO}_x$  at the  $\text{TiO}_2$ –Si interface already during the annealing at 250 °C. The  $\text{SiO}_x$  layer can either introduce defect states and recombination, or it affects the total charge of the thin film and thus weakens field-effect passivation. This is contrary to the literature where the presence of a thin  $\text{SiO}_x$  layer has been shown to improve the passivation.<sup>27,28</sup>



Earlier studies (summarized in Table S2, ESI<sup>†</sup>) have shown that the Si surface passivation quality by ALD TiO<sub>2</sub> thin films depends on the post-deposition thermal treatment. Therefore, the impact of the annealing on the  $S_{\text{eff}}$  of the samples is studied. The samples are annealed at 250 °C (Fig. 2b) and 300 °C (Fig. 2c) for different durations. The results show that the as-dep. TiO<sub>2</sub> grown on both HF-treated p- and n-Si substrates results in the lowest SRV while the annealing significantly enhances the SRV for all the samples. However, with annealing, a thermally introduced interfacial SiO<sub>x</sub> layer forms in between the TiO<sub>2</sub> and Si which seems to prevent the further degradation of the lifetime. This leads to a situation where actually after the annealing, the SRV for samples that initially had RCA2 SiO<sub>x</sub> at the interface is lower than the SRV for samples that initially had no SiO<sub>x</sub> at the TiO<sub>2</sub>–Si interface as shown in Fig. 2b. Furthermore, after annealing at 300 °C for extended durations up to 90 minutes, both HF-treated TiO<sub>2</sub>/n-Si and TiO<sub>2</sub>/p-Si samples show a similar increment in the SRV as shown in Fig. 2c. This observed trend is consistent with prior research, *e.g.*, carried out by Mochizuki *et al.*<sup>20</sup> and Liao *et al.*,<sup>29</sup> which attributes the increase in the SRV in the case of amorphous TiO<sub>2</sub> coatings to the increase in the interfacial defect density upon the formation of SiO<sub>x</sub> at the TiO<sub>2</sub>–Si interface already during thermal annealing at 250 °C. Therefore, it is evident that the surface passivation quality started to degrade already at the thermal treatment temperatures that were not sufficiently high to induce TiO<sub>2</sub> crystallization but at a temperature where diffusion of the dopants and impurities typically precedes the phase transition. This was confirmed by the Raman spectra of the samples after ALD and after 300 °C 90 min annealing (Fig. S10, ESI<sup>†</sup>) where no TiO<sub>2</sub> crystalline peaks (anatase or rutile) are observed. It is suggested that impurities in the ALD TiO<sub>2</sub> film originating from the ALD precursors, especially H can have a significant effect on the surface passivation.<sup>29,40</sup>

Fig. 3 presents measurements of the Si surface barrier height ( $V_{\text{sb}}$ ) using the Kelvin-probe method after varying annealing temperatures and durations. In TiO<sub>2</sub>/n-Si sample series, both with and without HF-treatment, a strong negative  $V_{\text{sb}}$  is obtained which remains stable even when the samples are annealed at 300 °C up to 90 minutes. Conversely, for TiO<sub>2</sub>/p-Si sample series, both with and without an HF-treatment,  $V_{\text{sb}}$  is slightly negative initially and then increases to slightly positive values as the annealing duration is increased. These differences

in  $V_{\text{sb}}$  values reflect the different electronic structures in p- and n-type Si.<sup>50</sup> This happens as the Fermi-levels are closely aligned for p-Si and TiO<sub>2</sub> which causes small  $V_{\text{sb}}$ , whereas the alignment of Fermi-levels for n-Si and TiO<sub>2</sub> causes a notable upward band bending, as indicated by the high negative  $V_{\text{sb}}$  values. The notable upward band bending should be harmful for electron transport into TiO<sub>2</sub> from Si and even result in a depletion of electrons at the n-Si surface, forming a hole-rich layer. The lowest SRV observed in Fig. 2 for HF-treated as-dep. TiO<sub>2</sub>/n-Si can be attributed to the strong field effect (inversion) passivation, whereas there is nearly no surface band bending on p-Si. This, coupled with the measured favorable lifetimes and low SRVs, indicates that all the as-dep. TiO<sub>2</sub> thin films have a good chemical passivation quality for both p- and n-Si substrates. The values without any annealing in Fig. 3a and b are slightly different because they are from different runs of experiments and the differences are within the given error limits. However, the measured  $V_{\text{sb}}$  remains at a similar level after the thermal treatment with increased temperature and duration. The increase of absolute  $V_{\text{sb}}$  values observed in certain cases, such as the annealing of the TiO<sub>2</sub>/n-Si sample for 5 minutes, suggests an enhancement in field-effect passivation. However, despite this improvement, the SRV experiences a significant increment. This implies that the increased SRV may stem from thermally induced interfacial defects rather than alterations in field-effect passivation.

### 3.2. Charge transfer through the TiO<sub>2</sub>/Si interface

For optimal device performance, most of the minority carriers should remain in Si and there should be only majority charge carrier transfer across the TiO<sub>2</sub>–Si interface. Therefore, to carefully analyze the charge transfer from Si to TiO<sub>2</sub> across the interface, contactless TR spectroscopy is utilized. Using this technique, one can measure the change in reflectance of the films upon photoexcitation. The samples were excited at 500 nm (with an energy density of 200  $\mu\text{J cm}^{-2}$ ) from the polished side of the samples to selectively generate the photocarriers in Si since TiO<sub>2</sub> does not absorb light in the visible region of the solar spectrum. The photogenerated carrier density can be calculated using  $N_0 = I \times \alpha \times e^{-\alpha x}$ , where  $I$  is the intensity of the incoming light,  $\alpha$  is the absorption coefficient, and  $x$  is the thickness at which the photocarriers are generated.<sup>33</sup> Therefore, at 500 nm excitation, approximately  $4.8 \times 10^9 \text{ e}^-/\text{h}^+$  pairs are generated at a depth of 1  $\mu\text{m}$  in Si. The total measured signal in the case of this study is given by  $\text{TR}_{\text{total}} = \text{TR}_{\text{Si}} + \text{TR}_{\text{TiO}_2}$ .

However, at 500 nm excitation, only Si is excited and any  $\text{TR}_{\text{TiO}_2}$  signal must originate from the carriers transferred from Si to TiO<sub>2</sub>, and hence is termed as the ‘‘CT signal’’. This signal is thus calculated by subtracting the estimated Si signal from the measured total signal. To examine how the charge carriers behave in Si upon photoexcitation at 500 nm, the temporal evolution of the TR spectra is observed for both pure Si substrates and TiO<sub>2</sub>/Si samples. Since the electron transfer from Si to the TiO<sub>2</sub> layer is investigated, we focus mainly on samples with the n-Si substrate where electrons are the

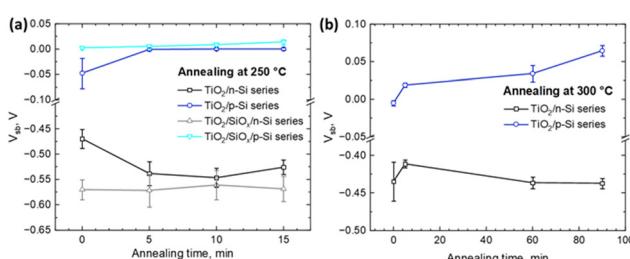


Fig. 3 Surface barrier height of different series of TiO<sub>2</sub>/Si heterojunctions deposited at 120 °C and further annealed at (a) 250 °C and (b) 300 °C for different time durations.



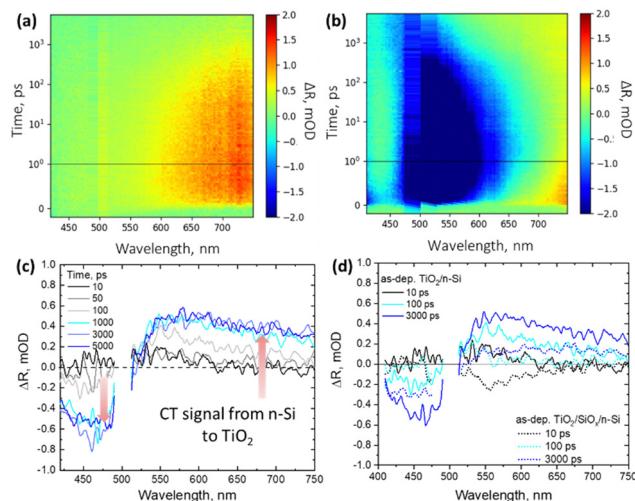


Fig. 4 Excitation of samples at 500 nm with  $200 \mu\text{J cm}^{-2}$  to obtain (a) TR spectra of the HF-treated bare n-Si substrate at different delay times, (b) TR spectra of the HF-treated as-dep.  $\text{TiO}_2/\text{n-Si}$  sample at different delay times, (c) extracted CT spectra in the HF-treated as-dep.  $\text{TiO}_2/\text{n-Si}$  sample where the arrows indicate electrons moving from n-Si to  $\text{TiO}_2$ , and (d) comparison of the extracted CT spectra for the HF-treated as-dep.  $\text{TiO}_2/\text{n-Si}$  sample and as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{n-Si}$  at different delay times.

majority carriers. Hence, the TR spectra of both HF-treated pure n-Si substrate and as-dep.  $\text{TiO}_2/\text{n-Si}$  samples are measured with excitation at 500 nm and the results are presented in the form of 2D maps as shown in Fig. 4a and b, respectively. For bare n-Si substrate, the TR spectra exhibit signals only in the positive range which decay as carriers diffuse from the surface to the bulk. However, with the addition of a 54 nm thick  $\text{TiO}_2$  thin film on Si, the interference pattern changes which in turn changes the TR spectra. Therefore, in the case of  $\text{TiO}_2/\text{n-Si}$  samples, at longer delay times,  $>500$  ps, the negative TR signal recovers partially and shows a blue shift while the positive TR signal starts evolving in the red region (600–750 nm) from 100 ps–5 ns in as-dep.  $\text{TiO}_2/\text{n-Si}$ .

To conduct a detailed analysis of the CT, we extract the TR spectra only related to the changes in  $\text{TiO}_2$  as a result of the CT

from Si to  $\text{TiO}_2$ . For this, any potential TR signal originating from Si is removed from the  $\text{TiO}_2/\text{Si}$  samples. As employed in our previous study,<sup>33</sup> we assume that the signal from 1 to 10 ps is entirely due to free carriers in Si which then decays as the photoinduced carriers diffuse away from the surface deeper into the bulk Si.

The carrier diffusion is assumed to be similar for both bare and  $\text{TiO}_2$  coated Si allowing us to estimate how the Si signal would behave if there was no CT to  $\text{TiO}_2$ . Therefore, in this case, the CT features are extracted from the TR spectra of as-dep.  $\text{TiO}_2/\text{n-Si}$  (Fig. 4b) and the bare n-Si (Fig. 4a). The extracted TR signal directly corresponds to the CT process and the strength of the TR signal,  $\Delta R$ , from  $\text{TiO}_2$  correlates directly with the number of transferred electrons, *i.e.*, an increase in the positive signal in the red region (600–750 nm) and an increase in the negative signal in the blue region (420–480 nm) after 100 ps are indicative of the transfer of charge carriers from n-Si to as-dep.  $\text{TiO}_2$  as shown in Fig. 4c. However, it can be observed that intensity of the TR signal reduces to nearly half, 0.25 mOD at 550 nm, in the case of as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples as compared to 0.5 mOD at 550 nm for HF-treated as-dep.  $\text{TiO}_2/\text{Si}$  samples as shown in Fig. 4d. It means that nearly half of the electrons get transferred in  $\text{SiO}_x$  containing Si samples as compared to  $\text{SiO}_x$ -free Si samples. The extracted CT spectra for all the other as-deposited samples (namely as-dep.  $\text{TiO}_2/\text{p-Si}$ , as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{p-Si}$ , and as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{n-Si}$ ) are analyzed similarly as shown in Fig. 4c and are presented in ESI,† Fig. S3–S5. Moreover, the extracted CT dynamics at different probe wavelengths enable us to compare the ultrafast responses of the different  $\text{TiO}_2/\text{Si}$  heterojunctions that experienced different pre-ALD chemical and post-ALD thermal treatments. Therefore, similar CT extraction analysis is applied to attain the decay dynamics of all the  $\text{TiO}_2/\text{Si}$  samples, and we see that the decay of bare n-Si clearly deviates from that of the  $\text{TiO}_2/\text{n-Si}$  samples after 100 ps which can be again attributed to the CT feature from Si to  $\text{TiO}_2$ . Fig. 5a shows the extracted CT dynamics of the HF-treated as-dep.  $\text{TiO}_2/\text{n-Si}$  sample at different probe wavelengths.

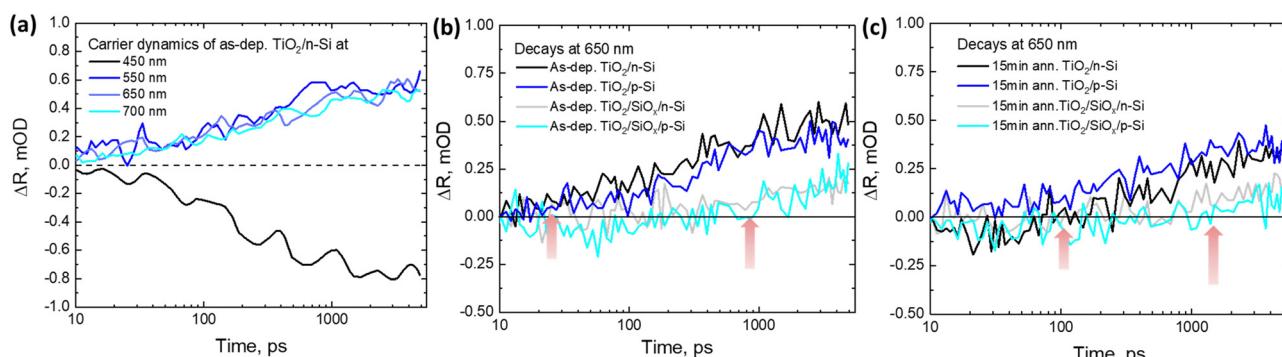


Fig. 5 (a) Extracted charge transfer dynamics after excitation of the HF-treated as-dep.  $\text{TiO}_2/\text{n-Si}$  sample at 500 nm (with  $200 \mu\text{J cm}^{-2}$  energy density) where the increase of the signal at different wavelengths is shown as a function of time which corresponds to the charge transfer signal increase at different wavelengths, and comparison of the extracted charge transfer signal increase at 650 nm probe wavelength for all the (b) HF-treated as-dep.  $\text{TiO}_2/\text{Si}$  samples, and (c) 15 minute annealed  $\text{TiO}_2/\text{Si}$  samples. The red arrow shows the charge transfer onset time where the charge transfer signal from Si to  $\text{TiO}_2$  first appears above the noise range.



To compare the CT dynamics of all the  $\text{TiO}_2/\text{Si}$  samples, the CT signal increase is compared at 650 nm probe wavelength as presented in Fig. 5b and c. The results show that the HF-treatment reduces the CT time from Si to  $\text{TiO}_2$  for both as-dep.  $\text{TiO}_2/\text{n-Si}$  and as-dep.  $\text{TiO}_2/\text{p-Si}$  samples and that the observed characteristic CT time (average time from where the CT signal increases from zero OD to the maximum OD on the 6 ns time scale of the TR measurement) is approx. 200 ps. However, for the as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples, the ones with chemical  $\text{SiO}_x$  at the interface, the CT time prolongs ten fold, *i.e.*, almost  $>2$  ns, as shown in Fig. 5b. Previously, we reported a somewhat faster CT time of 600 ps in as-dep.  $\text{TiO}_2/\text{SiO}_x/\text{Si}$  samples while a similar fast CT time of 200 ps was observed for a HF-treated  $\text{TiO}_2/\text{Si}$  samples.<sup>33</sup> The results also agree with the surface barrier height results as there is a larger barrier for electrons when there is a  $\text{SiO}_x$  layer. The photodynamics results also show that the CT signal does not keep increasing and saturates after approx. 1 ns. This occurs because charges accumulate near the  $\text{TiO}_2$  side of the interface due to the low carrier mobility in  $\text{TiO}_2$ , taking approximately 1  $\mu\text{s}$  to reach the surface,<sup>33</sup> shown in Fig. 6.

Hence, eventually, the CT process from Si to  $\text{TiO}_2$  is inhibited. In practical devices, this problem is typically addressed by making  $\text{TiO}_2$  thin enough (a few nm only) so that the carriers can reach the front surface despite the low mobility. As mentioned earlier, the samples were also annealed at 250 °C and 300 °C to investigate their thermal stability and its impact on the surface passivation. It can be observed that when the  $\text{TiO}_2$  films grown on both HF-treated p- and n-Si are annealed for 15 minutes at 250 °C, the characteristic CT time prolongs to almost 1.5 ns, as shown in Fig. 5c. The annealing induces the formation of interfacial  $\text{SiO}_x$  that was previously shown to increase the CT time to 370 ps with low-defect anatase  $\text{TiO}_2$  coating.<sup>33</sup> The prolonged CT time here can be rationalized by the differences between amorphous and crystalline  $\text{TiO}_2$ . While in crystalline low-defect  $\text{TiO}_2$  electrons transfer to the conduction band, in amorphous  $\text{TiO}_2$  electrons can transfer to the impurity mediated defect states that are strongly modified by the annealing, shown in Fig. 6.

This prolonged CT time in annealed samples is therefore suggested to originate from the introduction of thermally originated interfacial  $\text{SiO}_x$  at the  $\text{TiO}_2$ -Si interface which hinders the CT process, and also from a reduction in the amount of available defect states within annealed  $\text{TiO}_2$  as compared to the as-deposited amorphous  $\text{TiO}_2$ .<sup>33</sup>

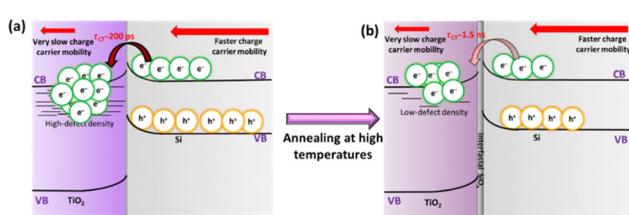


Fig. 6 Schematic of photoinduced interfacial charge transfer in (a) as-dep.  $\text{TiO}_2/\text{n-Si}$  and (b) 15 min annealed  $\text{TiO}_2/\text{n-Si}$  samples.

The increase in the CT time could be linked to the decreasing tunneling probability with increasing  $\text{SiO}_x$  barrier width. However, our optical instruments are not accurate enough to provide an estimate of the barrier thickness with sufficient accuracy for calculating the tunneling probability, which depends exponentially on the barrier thickness. The CT dynamics were also examined for HF-treated  $\text{TiO}_2/\text{n-Si}$  samples annealed at 300 °C for even longer durations, *i.e.*, for 60 and 90 minutes, to see the effect of higher temperature thermal treatment on the CT time. The results are shown in Fig. S6b in the ESI,<sup>†</sup> where it can be seen that the CT time prolongs even more, *i.e.*,  $>5$  ns.

Hence, it can be inferred that the samples exhibit limited thermal stability, consequently impacting the CT time and potentially impeding the efficiency of solar-to-electric conversion in Si-based PV devices. The characteristic CT times for all the HF-treated and untreated  $\text{TiO}_2/\text{n-Si}$  heterojunctions (both as-dep. and annealed at 250 °C for different durations) are summarized in Table 1 and the results for  $\text{TiO}_2/\text{p-Si}$  heterojunctions are presented in Table S3 in the ESI.<sup>†</sup> The results show that the CT times are strongly affected by the Si substrate pre-treatments, *i.e.*, the Si surface, and sample post-treatments, *i.e.*, a “thermally generated  $\text{SiO}_x$ ” layer at the  $\text{TiO}_2$ -Si interface. However, the effect of doping on the CT time cannot be observed clearly in the case of our study as signals are weak and the differences are in the noise range.

### 3.3. Impact of the annealing on $\text{TiO}_2$

To investigate possible annealing induced morphological changes in  $\text{TiO}_2$  thin films, AFM images of  $\text{TiO}_2/\text{n-Si}$  samples subjected to various annealing conditions were taken and the results for all the samples are shown in ESI,<sup>†</sup> Fig. S9. The results indicate that when the annealing is done at 250 °C for 5 to 15 minutes, the surface roughness increases only  $<0.1$  nm compared to the as-deposited surface. Annealing at 300 °C increases the surface roughness a bit more but the topography remains to depict amorphous characteristics as shown in Fig. 7a and b, thus indicating some degree of structural changes in the  $\text{TiO}_2$  films presumably due to the desorption of impurity atoms introduced due to precursors during deposition.

Moreover, we observe a correlation between the surface roughness and the  $S_{\text{eff}}$  values as shown in Fig. 7c where it can be seen that the  $S_{\text{eff}}$  increase is the most significant during the initial annealing, *i.e.*, when the as-dep. samples are thermally

Table 1 Characteristic charge transfer time from Si to  $\text{TiO}_2$  observed in  $\text{TiO}_2/\text{n-Si}$  heterojunctions annealed at 250 °C for different durations. The samples are excited at 500 nm with an excitation density of 200  $\mu\text{J cm}^{-2}$

| $\text{TiO}_2/\text{n-Si}$<br>(HF-treated series) | Characteristic<br>CT time | $\text{TiO}_2/\text{SiO}_x/\text{n-Si}$<br>(RCA2-treated series) | Characteristic<br>CT time |
|---|---------------------------|--|---------------------------|
| As-deposited                                      | 200 ps                    | As-deposited   | 2.5 ns                    |
| 5 min annealed                                    | 450 ps                    | 5 min annealed   | 4 ns                      |
| 10 min annealed                                   | 1 ns                      | 10 min annealed  | $>5$ ns                   |
| 15 min annealed                                   | 1.5 ns                    | 15 min annealed  | $>5$ ns                   |



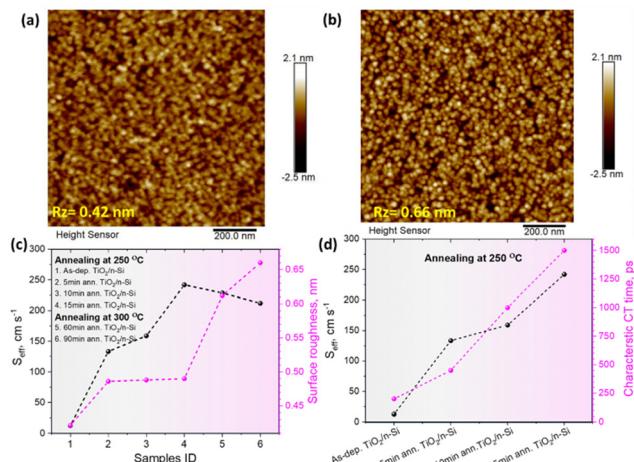


Fig. 7 AFM images of (a) as-dep.  $\text{TiO}_2/\text{n-Si}$ , (b) 90 min annealed  $\text{TiO}_2/\text{n-Si}$  at  $300^\circ\text{C}$ , (c) correlation of surface recombination velocity and surface roughness of the samples, and (d) correlation of surface recombination velocity and characteristic charge transfer times for HF-treated  $\text{TiO}_2/\text{n-Si}$  heterojunctions annealed at  $250^\circ\text{C}$  up to 15 minutes.

treated even for 5 minutes and after that it increases gradually for all annealed samples. It has been pointed out that the presence of H and Cl atoms in the as-deposited samples is favorable for surface passivation.<sup>29</sup> In our study, Cl originates from the  $\text{TiCl}_4$  precursor during the ALD growth at low temperature while H originates from both the  $\text{H}_2\text{O}$  precursor during ALD growth and HF dip prior to the ALD treatment. Also, the chemical  $\text{SiO}_x$  contains hydrogen in the form of hydroxyl groups. However, upon the annealing, the H and Cl atoms can desorb from the samples which decreases the passivation quality of all the annealed  $\text{TiO}_2$  p- and n-Si samples.<sup>12</sup>

Furthermore, to observe the effect of thermal annealing on the charge carrier dynamics in  $\text{TiO}_2$  films solely, the samples were excited at  $320 \text{ nm}$  by TR spectroscopy to selectively photoexcite the carriers in  $\text{TiO}_2$ .<sup>51</sup> The photodynamics of the HF-treated  $\text{TiO}_2/\text{n-Si}$  sample series is compared at  $600 \text{ nm}$  probe wavelength (Fig. S8, ESI†) and it can be seen that the lifetime of photocarriers in  $\text{TiO}_2$  does not improve when the samples are annealed for 5 to 15 minutes at  $250^\circ\text{C}$ . However, annealing of the samples at  $300^\circ\text{C}$  for 60 and 90 minutes slightly enhances the lifetime of the photogenerated carriers to  $\sim 0.1 \text{ ns}$ , but this is still less than the carrier lifetimes in crystalline  $\text{TiO}_2$  ( $\sim 4 \text{ ns}$ , ref. 51).

Nevertheless, this enhancement in the lifetimes of photocarriers in annealed  $\text{TiO}_2$  films is rather minor and might be attributed to the slight reduction in the recombination centers (less defects and intra-band gap states, Fig. 6b) in them as compared to the as-dep.  $\text{TiO}_2$  films.<sup>51</sup> This also suggests a slight reduction in the impurity related defects within  $\text{TiO}_2$  while maintaining their amorphous character as shown by the AFM images. To summarize, thermal annealing was found to improve the lifetimes of charge carriers generated within  $\text{TiO}_2$  films but were detrimental to the lifetime of carriers photogenerated within Si. The effect should be even more pronounced for the annealed samples that induce crystallization of  $\text{TiO}_2$  films.

### 3.4. Correlation of the surface passivation with the CT time through the $\text{TiO}_2/\text{Si}$ interface

All the as-dep.  $\text{TiO}_2$  films grown on HF-treated n-Si substrates show the minimum CT time of 200 ps as shown in Fig. 6.  $\text{TiO}_2$  is commonly used as an electron transport layer in various optoelectronic devices which means that it should keep accepting electrons from Si. However, our measurements show that the CT signal does not keep increasing and saturates after approx. 1 ns as shown in Fig. 5b and c. This happens as the transferred electrons fill up all the available energy states in the CB of the  $\text{TiO}_2$  and instead of moving to the  $\text{TiO}_2$  surface, the charges start accumulating at the  $\text{TiO}_2$  side of the interface because of the low carrier mobility in  $\text{TiO}_2$ .<sup>33</sup> This leads to inhibition of further acceptance of electrons in  $\text{TiO}_2$  from Si and thus, the CT stops. This contributes to the field effect passivation in  $\text{TiO}_2$ -Si interfaces and the best passivation quality was obtained for samples showing the highest carrier saturation level. Although the Kelvin-probe found similar band bending regardless of the annealing time for  $\text{TiO}_2/\text{n-Si}$  samples, these measurements are carried out under intense illumination and may saturate the  $\text{TiO}_2$  layer even with a slow CT process. Also, the as-dep. samples are rich in H and Cl impurities which further improves the chemical surface passivation at the  $\text{TiO}_2$ -Si interface. However, it should be noted that the CT dynamics is sensitive to even subtle differences at the  $\text{TiO}_2$ -Si interface and within  $\text{TiO}_2$ , and a direct correlation is observed between the SRV and the CT process as a result of annealing, as shown in Fig. 7d. For instance, annealing the HF-treated samples at  $250^\circ\text{C}$  even for 15 minutes introduces interfacial  $\text{SiO}_x$  and induces desorption of the precursor traces and impurities from the amorphous  $\text{TiO}_2$  coating which in turn prolongs the CT time to 1.5 ns. Since passivation decreases and the CT time gets prolonged, these annealed samples are not suitable for achieving efficient performance in solar-to-energy conversion devices.

## 4. Conclusions

This study investigates  $\text{TiO}_2/\text{Si}$  heterojunctions, exploring the impact of pre-ALD chemical and post-ALD thermal treatments on interfacial  $\text{SiO}_x$  layer formation, the  $\text{TiO}_2$  film composition, and the structure. This study examines surface passivation through effective carrier lifetime measurements and investigates CT dynamics using ultrafast transient reflectance spectroscopy. Photocarriers are selectively generated in Si at  $500 \text{ nm}$  excitation to analyze CT across the  $\text{TiO}_2$ -Si interface. Findings reveal that HF-treated  $\text{SiO}_x$ -free n-Si with as-deposited  $\text{TiO}_2$  exhibits the highest effective lifetime of  $1.23 \text{ ms}$  due to the bifunctional passivation of the surface combining both chemical and field effect passivation mainly caused by the precursors especially H impurities. Also, this sample exhibits the fastest CT time from Si to  $\text{TiO}_2$ , within 200 ps, which is mainly due to the absence of interfacial  $\text{SiO}_x$  which causes hindrance in the CT. Moreover, annealing increases the surface recombination velocity, possibly due to structural changes and precursor impurity desorption. The presence of the  $\text{SiO}_x$  layer,



whether chemically or thermally induced, increases the CT time and decreases the number of transferred carriers, adversely affecting the device performance. This research suggests potential for developing TMO-based passivating layers with improved charge transport properties and provides a framework applicable to other semiconductor surfaces and interfaces for understanding time-resolved photoinduced changes and photodynamics.

## 5. Materials and methods

### 5.1. Scanning electron microscopy

For the thickness estimation of  $\text{TiO}_2$  thin films deposited by ALD, cross-sectional SEM images of the samples were taken by using a FEG Zeiss Gemini 500 SEM microscope in secondary and back scattered electron modes with an accelerating voltage of 3 kV and a working distance of 5 mm.

### 5.2. AFM

To assess the topography of  $\text{TiO}_2$  thin films, atomic force microscopy images of the samples were taken by using AFM Bruker Icon in tapping mode.

### 5.3. Steady state reflectance spectroscopy

The steady state reflectance spectra of the  $\text{TiO}_2/\text{Si}$  samples were measured using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. The measurements were carried out in the reflectance mode using a 'Specular Reflectance Attachment for 5° Incidence Angle' accessory with the spectrophotometer setup. Aluminium coated mirrors were used as reference mirrors. The spectra were recorded from 300 to 1200 nm.

### 5.4. The injection-dependent effective lifetime $\tau_{\text{eff}}$

The injection dependent effective lifetime was measured from the quarters by the contactless quasi steady-state photoconductance (QSSPC) method by using Sinton WCT-120 at room temperature. The software version for measurement and analysis is v5.72.0.10. For high lifetime ( $>100 \mu\text{s}$ ) samples short-flash and transient analysis modes are used, while for low lifetime ( $<100 \mu\text{s}$ ) samples long flash and generalized analysis modes are used. The reported lifetime was under an injection level of  $1 \times 10^{15} \text{ cm}^{-3}$ .

### 5.5. Surface barrier height

The surface barrier height was determined using a Semilab PV-2000A to execute the Kelvin-probe method. Measurements of the contact potential difference between the wafer and a reference electrode were conducted under intense illumination ( $V_{\text{CPD}}^{\text{light}}$ ) and in complete darkness ( $V_{\text{CPD}}^{\text{dark}}$ ), and the surface barrier height ( $V_{\text{sb}} = V_{\text{CPD}}^{\text{dark}} - V_{\text{CPD}}^{\text{light}}$ ) was determined based on the difference between the two lighting conditions. It was averaged from an area of  $20 \times 20 \text{ cm}^2$  with a measurement step of 5 mm.

### 5.6. Transient reflectance spectroscopy

Ultra-fast time-resolved pump-probe spectroscopy was used in reflectance mode to determine the optical properties of the  $\text{TiO}_2/\text{Si}$  samples. The fundamental laser pulses were generated *via* a Ti:Sapphire laser (Libra F, Coherent Inc., 800 nm, approx. 100 fs pulse width, repetition rate 1 kHz). 90% of the fundamental beam was directed onto an optical parametric amplifier (Topas C, Light conversion Ltd) to produce the desired excitation wavelength (320 nm and 500 nm in our case), approximately 1 mm beam diameter at the sample, attenuated up to  $200 \mu\text{J cm}^{-2}$ . 10% of the fundamental laser was delivered to the motorized stage (delay line) and then to a 2 mm cuvette with water to generate continuum white light for probe pulses. The probe light was split into the reference and signal beams. The absorbance change was measured in chopper mode which is synchronized with fundamental laser pulses. The samples were excited at 320 nm and 500 nm to selectively excite  $\text{TiO}_2$  and Si, respectively.<sup>33</sup> The spectra were averaged over 3000 pulses for each delay time.

## Conflicts of interest

There are no conflicts to declare.

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